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Role of the Interfacial Interactions from an Adjacent Wall on Polymer Diffusion JIHOON CHOI, Department of Materials Science and Engineering, Chungnam National University, NIGEL CLARKE, Department of Physics and Astronomy, The University of Sheffield, KAREN WINEY, Department of Materials Science and Engineering, University of Pennsylvania, JEFFREY METH, DuPont Nanocomposite Technologies, Central Research & Development, RUSSELL COMPOSTO, Department of Materials Science and Engineering, University of Pennsylvania — The tracer diffusion of deuterated polystyrene (dPS; $M_n = 23 - 1866$ kg/mol) with a thickness (l) is measured diffusing away from hydroxyl-terminated, phenyl-terminate, and PS-grafted silicon substrates. For a hydroxyl-functionalized substrate, short polymer chains $(M_n = 23 \text{ and } 49 \text{ kg/mol}; l >> R_g)$ exhibit a diffusion coefficient that is comparable to bulk PS, whereas long polymer chains $(M_n = 532 \text{ and}$ 1866 kg/mol; $l < R_q$) are significantly slower than the bulk case. This slowing down is consistent with the observation by Zheng et al. [1]. In particular, bimodal diffusion coefficient was observed for intermediate molecular weight $(M_n = 168 \text{ kg/mol}; l)$ $\sim R_q$). For phenyl-functionalized and PS-grafted substrates, no significant differences in the diffusion coefficients are observed although long polymer chains showed a moderate slowing down. These experiments demonstrate that the polymer diffusion of thin, confined films ($\sim R_{\rm g}$) away from the substrate is determined by the friction due to surface-monomer contacts, and is sensitive to the chemical state of the substrate, providing a new insight into a role of the interfacial interactions on polymer dynamics.

[1] X. Zheng, et al., *Phys. Rev. Lett.*, 74, 407 (1995).

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